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Atmospheric Chemistry and Physics
Discussions

Interactive comment on "Photo-degradation of atmospheric chromophores: type conversion and changes in photochemical reactivity" *by* Zhen Mu et al.

Anonymous Referee #2

Received and published: 24 December 2020

The manuscript 'Photodegradation of atmospheric chromophores: type conversion and changes in photochemical reactivity' provides results on the photochemical aging of atmospheric aerosols. The results include OC/EC analysis, parallel factor (PARAFAC) analysis of excitation-emission matrices, and photosensitization of singlet oxygen with each measured as a function of solar irradiation. The results are of interest and merit eventual publication in the atmospheric chemistry literature, however, the novelty, writing, and presentation require significant improvement and does not meet the standard for publication in Atmospheric Chemistry and Physics in its current state. My comments are outlined below.

General comment: The manuscript would benefit greatly from a substantial revision to improve the writing quality (see minor comments for extensive recommended changes), conceptual framework, and referenced literature, to increase the readability of this work.

Major comments: 1) The title of this manuscript could be revised to remove the 'type conversion' terminology which is ambiguous and not commonly used. I would recommend making it more explicit that you are talking about oxidation by revising to: Photodegradation of Atmospheric Chromophores: Changes in Oxidation State and Photochemical Reactivity.

2) In the first paragraph of section 3.2, the results on the decrease in absorbance vs. fluorescence (or TFV) are not well separated and it is extremely difficult to separate when the authors are referring to absorbance or the fluorescence of these. It appears decay constants are provided for TFV but nor for absorbance.... Do the photolysis decay kinetics differ significantly for the chromophores vs. fluorophores? Or does the absorbance decay at the same rate as TFV?

3) What are the estimated atmospheric photolysis lifetimes including the factor of 1.2-1.3 mentioned in Sec. 2.2? Also according to Figure S1 in the supplement, your light source has almost no flux from 300-350 nm where the aerosols sample absorb most strongly and differs substantially from the solar spectrum. This should be addressed at some point in the manuscript.

4) On pages 8-9, the impacts of photolysis on the EEMs and individual components could be discussed in much more detail with comparison to more literature. Here are some additional references on this topic:

Murphy, K. R.; Timko, S. A.; Gonsior, M.; Powers, L. C.; Wünsch, U. J.; Stedmon, C. A. Photochemistry Illuminates Ubiquitous Organic Matter Fluorescence Spectra. Environ. Sci. Technol. 2018, 52 (19), 11243–11250

Harrison, A. W.; Waterson, A. M.; De Bruyn, W. J. Spectroscopic and Photochemical Properties of Secondary Brown Carbon from Aqueous Reactions of Methylglyoxal. ACS Earth Space Chem. 2020, 4 (5), 762–773.

5) In Figure 3A, the absorbances of WSOM and WISOM are nearly identical in the POA samples but differ by a factor of 10 in ambient PM. Is this a genuine difference in optical properties of these fractions i.e. does the water-soluble fraction actually absorb much more strongly than the water-insoluble fraction? This would be in contrast to previous brown carbon literature worth discussing in the manuscript. The use of mass absorption efficiency (MAE) is mentioned in the Supplement but not in the manuscript.

6) Are the WSOM and WISOM combined for the PARAFAC analysis? I would expect that there would be some differences in the fluorophores present in each fraction. See this recent ACP paper where there are clear differences in the water-soluble and methanol-soluble fractions:

J. Tang, et al. "Molecular compositions and optical properties of dissolved brown carbon in biomass burning, coal combustion, and vehicle emission aerosols illuminated by excitation–emission matrix spectroscopy and Fourier transform ion cyclotron resonance mass spectrometry analysis" Atmos. Chem. Phys. 20, 2513-2532, 2020.

7) Tabulation of the relative changes in each of the components in Figure 4B-C would improve the presentation of the results. This is information is all packed into the paragraph starting at Line 222 and is difficult to parse.

8) The paper demonstrates that low energy triplets are the main precursor for singlet oxygen , but do very high energy triplets form singlet oxygen with less efficiency in general? It would seem intuitive to me that when the energy gap between singlet and triplet COM is large, the photosensitization reaction will be less efficient.

9) Implication section is short and lacks significance or contextualization in the large amount of literature on the photochemical oxidation of chromophoric organic matter in

atmospheric aerosols.

Minor comments:

Chromophoric Organic Matters should be 'matter' instead of 'matters'. Consider how making this change will impact verb conjugation

Line 9: Change 'Furtherly' to 'Furthermore'

Line 12: Change 'particle' to 'particulate'

Line 15: Change 'result also enunciate' to 'results also highlight'

Line 30: Change 'improve' to 'is necessary for'

Line 38: Change 'Photochemistry have' to 'Photochemistry has'

Line 101: Change 'time' to 'times'

Line 127: Change 'analyzed' to 'measured'

Line 131: Change 'excitation' to 'emission'

Line 134: Change 'chromophores' to 'fluorophores'

Line 176: Change 'photolysis' to 'photolyze' or rephrase sentence to 'undergo partial photolysis'

Line 179: Change 'result' to 'results'

Line 186: Change 'Contrast with' to 'In contrast to'

Fig. 2b: Heading says 'Ambint PM' rather than 'Ambient PM'

Line194-195: Change 'represent an obvious decreasing trend due to aerosol photolysis' to 'significantly decrease during aerosol photolysis'

Line 197: Change 'subduction' to 'decay'

Line 210: Change ‘photolysis’ to ‘photolyze’

Line 208-210: Sentence that begins with ‘The low attenuation result from COM’ is unclear and needs revision

Line 219: Change ‘chromophores’ to ‘fluorophores’

Line 220: Change ‘identified as’ to ‘associated with’

Line 243: Change ‘show’ to ‘shows’

Line 243: Change ‘do not significant affect’ to ‘does not significantly affect’

Line 260: Change ‘through the approach of’ to ‘using’

Line 261: Change ‘EPRs’ to ‘EPR’

Line 267: Change ‘increase by 3 times’ to ‘increases by a factor of 3’

Line 277: Line 176: Change ‘do’ to ‘does’

Line 278: Change ‘The mechanism is same as’ to ‘The mechanism is the same as the’

Line 285: Change ‘disappear’ to ‘disappears’

Line 288-289: Consider changing ‘restraining’ to ‘attenuating’ or ‘inhibiting’. ‘Restraining’ is an odd word to use for this.

Line 291: Change ‘prove’ to ‘show’

Line 293: Change ‘prove’ to ‘study’

Line 305: Change ‘reflect’ to ‘reflects’

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